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ZETA POTENTIAL IN CERAMIC INDUSTRY

M. Lecuit



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ZETA POTENTIAL IN CERAMIC INDUSTRY¹

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Introduction

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The zeta potential has already been recognized for a very long time as being the basic principle governing the stability of colloidal solutions.

Nevertheless, numerous difficulties encountered up to now in relation to its practical applications and directly applicable industrially have led us to restore its interest in the ceramic realm.

We will see later that this is the zeta potential, recalled more until now in all the works carried out and published to this day, this notion could only be applied on:

- argillaceous solutions -several ppm per liter-and not on slips-density going up to 1800 g per liter;
- elemental suspensions, that is to say only including very limited number of colloidal species.

We are a long way from a ceramic slip.

Nevertheless, we hope that a more progressive and more logical step will allow us to attribute to ceramic slips a significant and useable value of the zeta potential.

This study thus proposes for an objective not only of restoring the zeta potential notion, but of defining its interests in the ceramic realm.

¹ Study accomplished during Student-Engineer training at the Ceramic French Society.

* Numbers in the margin indicate pagination in the foreign text.

In order to do this and for a first time, we have chosen to treat primarily:

- argillaceous primary materials;
- argillaceous primary materials + deflocculant;
- mixtures in variable concentrations of these various constituents.

1. Zeta Potential: Condensed Bibliography

Clays constitute a typical strong case where, in suspension within water, the particles which compose it possess a distinct electrical charge, most often negative.

The electroneutrality of the suspension is ensured by compensating for these charges by ions of opposite sign. In electrolytic solutions, this phenomenon has the consequence of locally modifying the ionic concentrations in solution as a result of the phenomenon of coulomb nature interaction. For clays, the study of these interactions is very significant. The colloidal behavior of the mineral is in major part determined by the action of the particles on the structure and the composition of the liquid which surrounds them. .

11. Zeta Potential

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111. Definition

Argillaceous products in suspension within aqueous solutions present an aggregate negative charge. Consequently, they surround a certain number of ions of opposite sign, spreading over a double layer, in a manner to respect the electroneutrality of the system.

Plate 1 diagrams the structure of this double layer by considering the variation of the electrical potential Ψ as a function of the distance x of the particle.

It is thus constituted:

- of the particle-solution interface-potential Ψ_0 ;

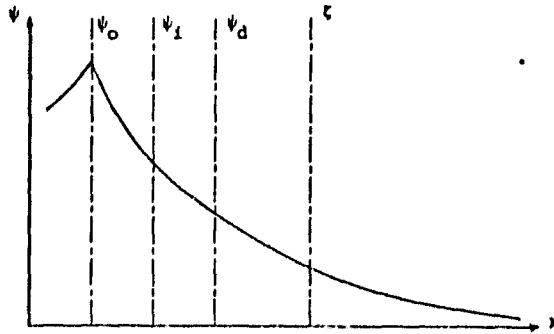


Plate 1. Structure of the double layer at the mineral particle-solution interface.

- of the interior plane of Helmholtz or fixed layer-potential Ψ_1 , which the theory defines as being in a plane parallel to the surface and the geometric locality of the ions adsorbed chemically by covalent or Van der waals bonds, and dissolved;
- of the Gouy-Chapman diffuse layer whose potential plane Ψ' is the geometric locality of the hydrated ions in contact with the surface.

If through whatever process, we displace the liquid phase in relation to the solid phase or inversely, only the molecular layer directly in control with the surface remains steady; the potential of the plane which separates the fixed layer in relation to the mobile layer is called zeta potential or electrokinetic potential-designated ζ .

112. Gouy-Chapman Theory

This theory, amply developed, leads us to give a relatively simple mathematical expression allowing us to determine the value of the zeta potential.

Plate 2 diagrams the distribution of ions with the double layer following the model described by Gouy-Chapman and modified by Stern. The positive ions assemble around the solid negatively charged particle and distribute themselves:

- in a fixed layer bound to the solid;
- in a diffuse and mobile layer.

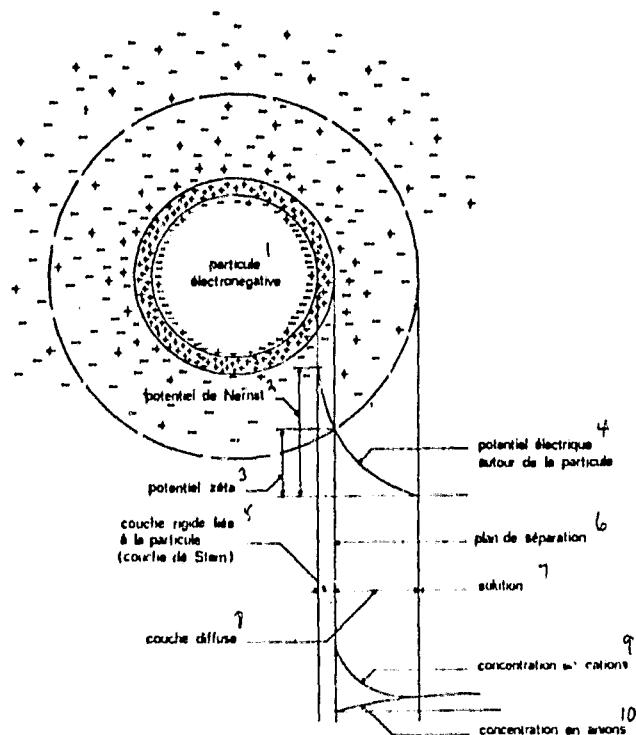


Plate 2. Zeta potential concept.

Key: 1-Electronegative particles 2-Nernst potential 3-Zeta potential 4-electrical potential around the particle 5-rigid layer bound to the particle (Stern layer) 6-Separation plane 7-solution 8-Diffuse layer 9-Concentration in cations 10-concentration in anions.

The value of the potential at the level of the fixed layer-mobile layer separation is a significant magnitude, accessible experimentally: the electrokinetic potential or potential ζ which accounts for the charge of the particle.

We determine experimentally the value of the potential ζ for the argillaceous particles from electrophoresis measurements. The displacement velocity of these negative particles within an electric field gives the electrophoretic mobility u_e , the theory of the phenomenon, developed by Helmholtz-Smoluchowski allows us to connect this value to the electrokinetic potential:

$$u_e = \frac{D\zeta}{4\pi\eta} \text{ where } \zeta = \frac{4\pi\eta}{D} u_e$$

where D and η represent respectively the dielectric constant and the viscosity of the intermicellar liquid.

We know well the principal way of variations of the potential ζ for numerous minerals, but relatively poorly for clays. Beside, knowledge of the electrokinetic potential is significant since the magnitude of the potential ζ conditions the interactions of electrostatic type between particles, and consequently, certain properties of the suspensions.

The potential ζ is even greater:

- when the electrical charge of the particle is large;
- when the thickness of the double layer is high;
- when the dielectric constant of the intermicellar liquid is low.

113. Zero Charge Point

The potential Ψ_0 at the surface of the solid is entirely determined by a thermodynamic equilibrium of adsorption governed by the law of Nernst:

$$\Psi_0 = A + \frac{RT}{F} \ln a^+ \quad \Psi_0 = B - \frac{RT}{F} \ln a^-$$

where A and B are constants, a^+ and a^- the activities of ions in solution.

Ψ could thus be rendered more positive or more negative by addition respectively of cations or anions. For each ion, there thus exists a concentration for which the surface potential Ψ_0 is zero, which we call ion concentration at zero charge point.

12. Argillaceous Suspensions: Their Stabilities

121. Argillaceous Suspensions

When we assume the charge due to the dissolution of the argillaceous micella into a macro-anion (clay-OH)⁻ and an H⁺ ion, or the adsorption of OH⁻ ions from the aqueous medium along the cleavage planes and more particularly along the lateral fractures of the crystal, a perfectly purified clay, that is to say only including H⁺ and OH⁻ ions, such that it is defined under the word clay H⁺-clay-OH⁻, it appeared

to us as constituted of lined micella of OH^- ions around which gravitate the positively charged H^+ ions which are attracted by the negative charge of the surface of the nucleus and which ensures the electrical neutrality of the assemblage.

This neutrality is represented by:

$$[\text{H}^+] [\text{OH}^-] = \text{constant} \text{ (law of mass action)}$$

122. Stabilities of Argillaceous Suspensions

An argillaceous suspension finds itself constituted by a multitude of these elemental particles surrounded by their lyosphere floating in free water. Each of these is attracted by two antagonistic forces: on the one hand, they mutually repel since they are charged with negative electricity; on the other hand, they undergo forces of molecular attraction (Van der Walls forces) which develop when they come into immediate proximity under the effect of Brownian motion. If at the time of the approach of two or several particles, the potential gradients are such that the electrostatic forces of repulsion take it before the forces of attraction become preponderant, there is repulsion and the suspension is stable: the clay is deflocculated or peptyzed. In the opposite case, the particles are attracted, forming aggregates: there is flocculation. Any modification of the ionic atmosphere, the charge of the particles or the dielectric constant by addition of acids, bases or salts is thus capable of modifying the conditions of stability of the suspension.

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In the case of a H-clay-OH clay, the only positive ions of the ionic atmosphere are the hydrogen ions. These are very small and slightly hydrated monovalent ions. They can thus crowd together around the negative micella in an ionic atmosphere of low thickness by constituting an extremely tight cloud. They are thus also capable of developing a high electrostatic field giving a steep potential gradient whose repulsive effect can only be felt at a very small distance, for which the Van der Waals forces can become preponderant. These clays thus will normally be flocculated. The deflocculated H-clay-OH clays

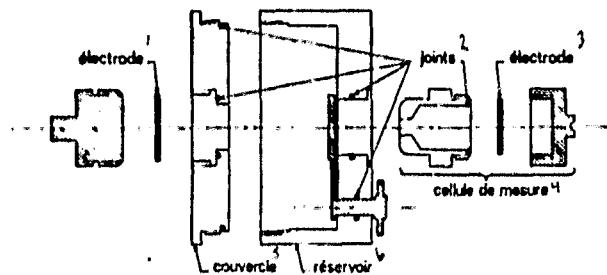


Plate 3a. Mass transport chamber.

Key: 1-electrode 2-Joints 3-Electrode 4-Measurement cell
5-Cover 6-Reservoir.

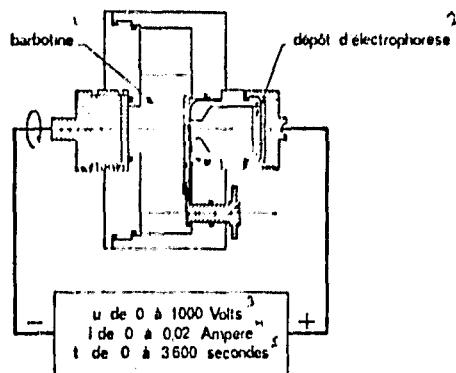


Plate 3b. Electrophoretic mass transfer analyzer.

Key: 1-Slip 2-Electrophoresis deposit 3-u from 0 to 1000
volts 4-i from 0 to 0.02 amperes 5-t from 0 to 3600 seconds.

obtained by electrodialysis are always in an unstable state and traces of acids or salt would induce their flocculation.

123. Correlation Between Electrokinetic Potential and Stability

We demonstrate that the stability of a colloidal suspension is even greater when its electrokinetic potential is large, which is easily understood by the definition itself of this potential.

To this end, we give the range of stability established by Thomas M. Riddick in the first volume of his work "Control of Colloid Stability through Zeta Potential", range which is confirmed experimentally.

Table 1.

Type	Potential
Maximum agglomeration and precipitation	from 0 to 3 mV
High agglomeration and precipitation	from +4 to -5 mV
Agglomeration threshold	from -10 to -15 mV
Dispersion threshold	from -16 to -30 mV
Medium stability	from -31 to -40 mV
Good stability	from -41 to -60 mV
Very good stability	from -61 to -80 mV
Excellent stability	from -81 to -100 mV

13. Correlation Between Zeta Potential and Rheologic Characteristics

A suspension with a given percentage of water—that is to say with given density—has its rheologic characteristics (apparent shearing velocity threshold) imposed by:

- the proportion of water "bound" to the particles, in the form of rigid hydrospheres, and the proportion of "free" water which ensures the mobility of the hydrospheres in relation to one another;
- the forces of attraction and repulsion of the particles, whose imbalance can lead to the formation of agglomerates of particles which then behave like single large-sized particles;
- the characteristics of the mineral in suspension, of which the specific surface is the most significant.

The practical incidence of the surface charge of the particles is the estimation of the original electrostatic forces exercised between particles in suspension. These forces condition certain properties of the clay-water mixture, such as viscosity and flocculation. Thus, at the zero charge point, the degree of flocculation is maximum, by compensation the degree of dispersion must be even better when the zeta potential is high.

The zeta potential allows a quantitative estimation of the repul-

sion forces active at the interior of the argillaceous + water suspension system. The higher the absolute value of the potential ζ , the smaller the relative value, the higher the forces of repulsion between the clay particles. It is the same with the stability of the suspension. In proportion that the absolute value of the potential ζ increases, we pass progressively from the maximum agglomeration states to the maximum stability states (see table 1 above).

The determination of the potential ζ thus allows attainment of an exact image of the state of more or less high stability of the colloidal system studied and consequently of its flocculation (or deflocculation) state.

It also appeared, and this is confirmed by numerous studies found in the bibliographies and done-among others-on oxide slips, that there exists a close parallelism between the curves of variation of the potential ζ and viscosity with variable electrolyte content, or pH (although certain electrolytes do not produce notable variation of pH). Thus, at the time of these studies, it had been established that there necessarily exists a maximum in the pH-potential curves. In agreement with the theory, this maximum corresponds to a minimum in the pH-viscosity curves. From this fact, a high Yield-Value must be associated with a high potential.

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On the other hand, a high potential ζ prevents strong attraction between the particles and leads, consequently, to a base velocity. The zeta potential is thus not an intrinsic characteristic of the mineral, but of the suspension formed by the mineral dispersed in the solution. It is thus variable with the nature of the dispersive liquid and with the pH of the suspension.

2. Theoretical Calculation of Zeta Potential

In order to account for electrokinetic phenomena, it is simply necessary to consider that the diffuse region of the double layer is at least in part mobile. When an external electrical field is applied

tangentially to a fixed surface, the mobile portion of the diffuse double layer disperses under the action of the forces acting on the excess of ionic charges contained at the interior. A constant flow velocity will be attained when the force exercised by the exterior field on the ions—thus on the liquid assemblage—will be exactly balanced by the friction forces arising from the velocity of the liquid.

Mathematical Relationship Between the Electrophoretic Velocity and Zeta Potential

The double layer must satisfy the Poisson equation:

$$\Delta \Psi = 4\pi \rho / D \quad (1)$$

where: Δ is the Laplace operator

Ψ is the localized double layer potential at a distance x from the same point

ρ is the spatial charge per unit of volume at the same point

D is the dielectric constant of the dispersive medium.

We consider telling from calculations to come that the liquid follows a laminar regime, that its viscosity η and dielectric constant D are uniform throughout the mobile part of the double layer, that the thickness of this last is small compared to the radius of curvature of the surface.

When an electrical field E is applied to each element of volume of the liquid layer of thickness dx , at a distance x from the surface, it creates a force:

$$F_1 = E \cdot \rho \cdot dx.$$

In permanent regime, the viscosity which allows us to carry along the liquid layer, contributes to displace the adjacent layers with different velocities.

The side of the layer at a distance x from the surface will be delayed by a force which can be expressed by:

$$f_x = -\eta \left(\frac{dv}{dx} \right)_x$$

where v is the velocity of the liquid.

The side at a distance $(x+dx)$ from the surface will be accelerated itself by a force:

$$f_{x+dx} = \gamma \left(\frac{dv}{dx} \right)_{x+dx}.$$

The resulting friction force on the curve in question is thus:

$$F_2 = \gamma \left(\frac{dv}{dx} \right)_{x+dx} - \gamma \left(\frac{dv}{dx} \right)_x.$$

At the equilibrium, the total force on the layer is zero, and consequently, it becomes:

$$E \rho dx - \gamma \left(\frac{d^2 v}{dx^2} \right)_x = 0 \quad (2)$$

By substituting in equation (2) the value of Ψ deduced from equation (1) and by placing it into the hypothesis of a flat surface, it becomes:

$$\Delta \Psi = \left(\frac{d^2 \Psi}{dx^2} \right)$$

thus: $-\frac{ED}{4\pi} \left(\frac{d^2 \Psi}{dx^2} \right) = \eta \left(\frac{d^2 v}{dx^2} \right)$

By integrating this differential equation on the liquid assemblage, /24 since the separation plane is infinite, we obtain:

$$-\frac{ED}{4\pi} \left(\frac{d\Psi}{dx} \right) = \gamma \left(\frac{dv}{dx} \right) + C$$

The conditions at limits $(\frac{d\Psi}{dx})_{\infty} = 0$ and $(\frac{dv}{dx})_{\infty} = 0$ imply $C=0$.

We integrate again and it becomes:

$$-\frac{ED}{4\pi} \Psi = \eta v + C'$$

where: for $x \rightarrow \infty$, $\Psi = 0$ and $v = v_e$ electrophoretic velocity on the separation plane $v = 0$ and $\Psi = \zeta$.

We thus obtain the simple relationship:

$$v_e = \frac{D \epsilon \xi}{4 \pi \eta}$$

If we consider besides that the field E is applied perpendicularly to a cross-section A of the liquid, it becomes by application of Ohms Law:

$$E = \frac{i}{A \lambda}$$

where: λ is the specific conductance of the liquid

i is the intensity of the current crossing the section considered.

We thus obtain:

$$v_e = \frac{D i \xi}{4 \pi \eta A \lambda}$$

3. Apparatus Used at the S.F.C. Laboratory

31.

The manipulations of this apparatus have been made conforming to the joint instruction book, instructions completed by studies of the following bibliographic references:

- Depreatere, P., "Electrophoretic Mass Transfer Analyzer", Measurements, 1975;
- S.F.C. (J.P.C.), "Study of the SFC Zetameter instruction book", Study 106, reference 19760531.

32. Filling of the Measurement Cell

Despite all the precautions taken and all the care given to measurements, there generally continues to exist air within the slip contained in the measurement cell. It can have two origins:

- air included following agitation (micro-bubbles);
- but also and above all air imprisoned during filling of the cell, imprisoned due to the strong viscosities of certain slips.

Consequently, it is desirable in advance to deal with any measure of controlling vigilantly that the cell is effectively well filled.

For this, it suffices to rapidly calculate the apparent density of the slip contained in the cell. We operate in this order:

-weigh the assemblage (empty mounted cell+capillary) perfectly dry- P_1 ;

-fill this same assemblage with distilled water of which we will note the temperature T ;

-Weigh it- P_2 ;

- $\Delta P = P_2 - P_1$ weight of water;

- $T^{\circ}\text{C} \rightarrow \rho$ water;

-deduce from it the assemblage volume (empty cell+capillary)

$$V = \Delta P / \rho \text{ cm}^3.$$

These operations are made once each, then:

-fill the slip of the assemblage (cell+capillary), theoretical density ρ ;

-weigh it- P_3 ;

-deduce from it the density of the slip

$$\rho' = (P_3 - P_1) / V.$$

If the difference $(\rho - \rho')$, difference obviously by defect, is greater than 5%, complete refilling of the cell.

In the opposite case, pursue the manipulation as indicated in the instruction:

-as soon as possible after the stop of the application of the electrical field, close the shutter of the cell and withdraw the assemblage (reservoir+cell) from its measurement support;

-extract the cell;

-ensure that it does not contain any air bubbles-for this, tap it softly;

-adjust the level of the suspension within the cell with the assistance of the capillary tube.

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322. Remark

The measurements of the electrophoretic velocity and potential ζ

are made on argillaceous suspensions and slips, suspensions and slips which can be flocculated or deflocculated.

In the first case, the dispersive liquid, generally distilled water, is perfectly defined, at a given temperature, by its three characteristics:

- density;
- viscosity;
- dielectric constant.

In the second case, the dispersive liquid is a solution of electrolytes in distilled water (silicates, carbonates, ...). If these characteristics, density and viscosity, are in first approximation those of the distilled water, its "dielectric constant" characteristic extends further than that of distilled water when the electrolyte concentration is great.

This phenomenon is expressed by the law of Lichtenecker:

$$\ln D = \gamma_1 \ln D_1 + \gamma_2 \ln D_2 + \dots = \sum_i^n \gamma_i \ln D_i$$

where: D is the dielectric constant of the assemblage;

γ_i is the concentration in volume of the electrolyte i ;

D_i is the dielectric constant of the electrolyte i .

We observe, from the appearance of this expression, that generally the influence of the addition of whatever electrolyte is negligible (γ_i very small before γ_1 of distilled water).

Nevertheless, in order to not introduce new errors, we will endeavor to only make these measurements after total adsorption of the electrolyte by the argillaceous particles. It is thus that a delay of seven days was observed between preparation and measurements on deflocculated slips with the assistance of sodium silicate Na_2SiO_3 .

33. Calculation Method

331. Calculation Data

- Resistance of the argillaceous suspension: $R(\Omega)$... measured;
- Initial temperature of the suspension: t_1 ($^{\circ}\text{C}$) ... measured;
- Density
- Viscosity
- Dielectric constant
- Density of the sample: ρ_s (g/cm^3) ... given;
- Conductivity constant of the cell: K (cm^{-1}) ... given (rating)
- Current: $i(\text{A})$... constant⁽¹⁾
- Duration: $t(\text{s})$... constant⁽¹⁾
- Button positionned on +test
- Initial weight of the capillary cell-sample assemblage: $P_1(\text{g})$... measured;
- Final weight of this same assemblage: $P_2(\text{g})$... measured;
- Variation of weight P of the cell: $P(\text{g}) = P_2 - P_1$.

332. Calculation

$$\phi^{(2)} = \frac{(\text{Weight of the solid fraction } \rho_s)}{(\text{Weight of solid fraction } \rho_s) + (\text{Weight of liquid fraction } \rho_1)}$$

$$\text{-Voluminal solid fraction: } \phi \\ \omega_e = \frac{P \times K}{R \times t \times i \times (1-\phi) (\rho_s - \rho_1)}$$

-Electrophoretic mobility: ω_e ($\text{cm}^{-1}/\text{v cm}^{-1}$) (The electrode of the cell being positive (+test), the particles migrate within the cell, these last are negatively charged and, by convention, the electrophoretic mobility is negative).

-Zeta potential: $\zeta(\text{V})$

(1) Fixed arbitrarily, respectively at $5 \cdot 10^{-3}$ s and $3 \cdot 10^2$ s.

(2) Weight of the solid fraction and weight of the liquid fraction being the basic elements for the selection of the slip density, here 1300 g/l.

$$\zeta = \frac{36 \cdot 10^{-4} \gamma_i \times \nu_e \times \eta}{D}$$

(The constant term contains an electrostatic voltage conversion into "practical" voltage).

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5. Studies of Argillaceous Suspensions

51. Products Used

511. Argillaceous Primary Materials

With the number of 3, they have been selected on the one hand because they are argillaceous, on the other hand and above all because by combining them in proper proportions, they reconstitute, in first approximation, the argillaceous phase of an industrial type slip (Slip I).

These are the following:

- Kaolin d'Arvor
- Ball Clay Hyplas 64
- Granger Clay No. 10.

512. Deflocculant

The deflocculant used is sodium silicate Na_2SiO_3 of the following standards and analysis:

-Sodium silicate	Na_2SiO_3
-Active product	100%

-Molecular mass	122.06 g
-Na ₂ O	50.80%
-SiO ₂	49.20%
-H ₂ O	0%

52. Preparation of Samples

The samples have been prepared as indicated in paragraph 41 of the instruction book.

We note however that:

- the slips are only made after a stay during 24 hours of the primary materials in the drying oven at -50°C (elimination of the water moisture);
- the sodium silicate, when there is deflocculation, is placed in solution in distilled water, constantly stirred, and not used until after complete dissolution;
- we have also endeavored, with care of comparison, to maintain constant time and velocity of stirring at the time of production of the slips;
- the density of the slips is controlled for possible adjustment by simple weight in a volumetric flask. A series of 5 measurements is then made on each slip.

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6. Measurements

The slips prepared as indicated above are allowed to rest respectively during 48 hours for non-deflocculated slips and one week for those deflocculated.

Previous stirring of 15 to 30 minutes according to the cases is done before the measurements.

The measurements are then carried out conforming to the instruction book.

Remark: Periodic calibration of the conductivity cell is desira-

ble for attainment of consistent values for the magnitudes R , v_e and ζ .

7. Results

71. Primary Materials Alone

711. Kaolin d'Arvor (2.618 g/cm³)

We will distinguish for this last:

- low density slips 1100, 1150, 1200, 1250 and 1300 g/l. Measurements possible on the S.F.C. zetameter without deflocculant;
- high density slips ≥ 1300 g/l for which addition of electrolyte is indispensable in order to carry out the measurements under perfect conditions, particularly filling of the cell.

The rate of deflocculant given in ppm relates to the weight of dried materials.

7111. Low Density Slips (table 2, plate 4)

The results obtained allow us to believe that the representative curves which result from them correspond to simple even degree mathematical equations, at least in the realm of densities explored.

We will restrict ourselves to an investigation of the second degree equations.

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It has led us to:

Potential ζ

$$\zeta = -5072.6 \cdot 10^{-4} P^2 + 1310.1 P - 856257.6$$

where: ζ is expressed in mV

P in g/l

Electrophoretic velocity v_e

$$v_e = -3597.71 \cdot 10^{-5} P^2 + 9303.6 \cdot 10^{-2} P - 60890.3$$

where: v_e is expressed in $10^{-4} \text{ cm s}^{-1} / \text{V cm}^{-1}$

P in g/l

TABLE 2. KAOLIN D'ARVOR
SLIPS: 1100, 1150, 1200, 1250, 1300 g/l

Na_2SiO_3 ppm	R_m Ω	μ_e $10^{-4} \text{ cm s}^{-1} / \text{V cm}^{-1}$	β 10^{-3} v
1100	15315	2,11	29,31
1150	10952	1,45	20,00
1200	8732	1,09	14,48
1250	7585	0,83	11,23
1300	6775	0,74	10,37

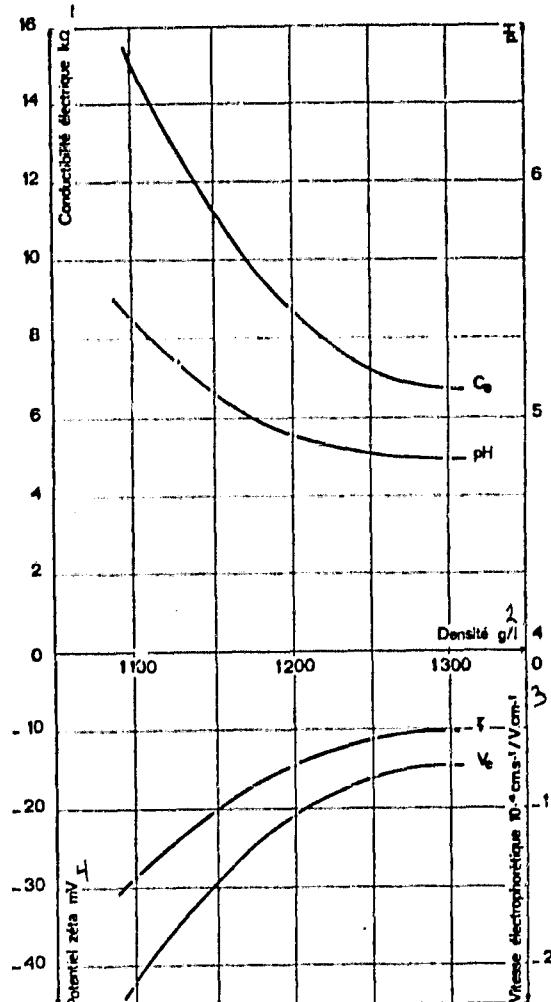


Plate 4. Kaolin d'Arvor.
Characteristics at low densities.

Key: 1-Electrical conductivity 2-Density 3-Electrophoretic velocity 4-Zeta potential.

Ohmic resistance

$$R = 2185.7 \cdot 10^{-1} P^2 - 5664.1 \cdot 10^{+2} P + 3737.2 \cdot 10^{-5}$$

where: R is expressed in
P in g/l.

7112. High Density Slips (tables 3, 4, and 5; Plates 5 to 7)

TABLE 3. KAOLIN D'ARVOR.
SLIPS: 1300 g/l

Na ₂ SiO ₃ ppm	R _m Ω	v _e 10 ⁻⁴ cm s ⁻¹ /V cm ⁻¹	f 10 ⁻³ V
0	6840,75	1,24	18,27
40	6143,75	1,27	18,56
100	6115,25	1,60	22,53
500	3776	2,93	41,75
1000	2775	3,32	46,47
2000	1680,25	3,52	50,90
3000	1087,50	3,65	53,00
4000	731,50	3,59	51,28

TABLE 4. KAOLIN D'ARVOR.
SLIPS: 1500 g/l

Na ₂ SiO ₃ ppm	R _m Ω	v _e 10 ⁻⁴ cm s ⁻¹ /V cm ⁻¹	f 10 ⁻³ V
500	2914	1,77	24,95
1000	2093,30	2,49	34,04
1500	1570,25	2,64	37,33
2000	1348,50	2,74	39,20
2500	1031,75	2,78	39,97
3000	784	2,82	39,58
4000	590,32	2,74	38,52

TABLE 5. KAOLIN D'ARVOR.
SLIPS: 1700 g/l

Na ₂ SiO ₃ ppm	R _m Ω	v _e 10 ⁻⁴ cm s ⁻¹ /V cm ⁻¹	f 10 ⁻³ V
1500	1458,25	2,21	30,87
2000	1028	2,49	34,25
2500	826	2,61	35,97
3000	646,05	2,76	37,92
4000	456,35	2,67	36,02

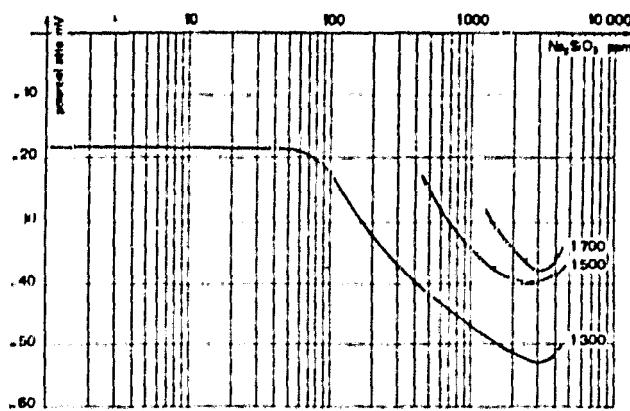


Plate 5. Kaolin d'Arvor.
Deflocculation curves.

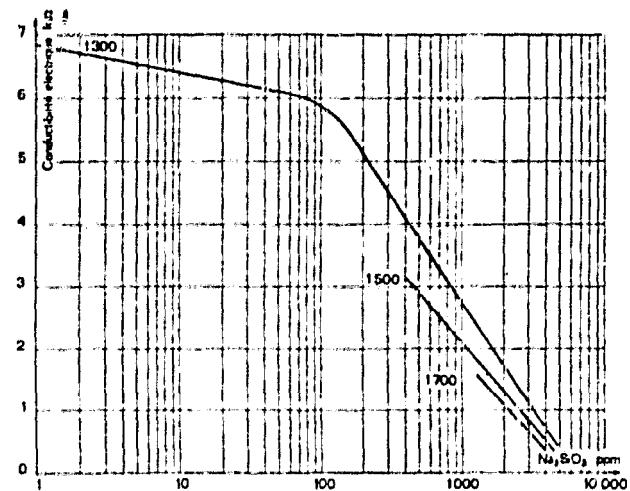


Plate 6. Kaolin d'Arvor.
Electrical conductivities.

Key: 1-Electrical conductivity.

712. Ball Clay Hyplas 64 (2600 g/cm³) (plates 8 to 10; table 6)

/29

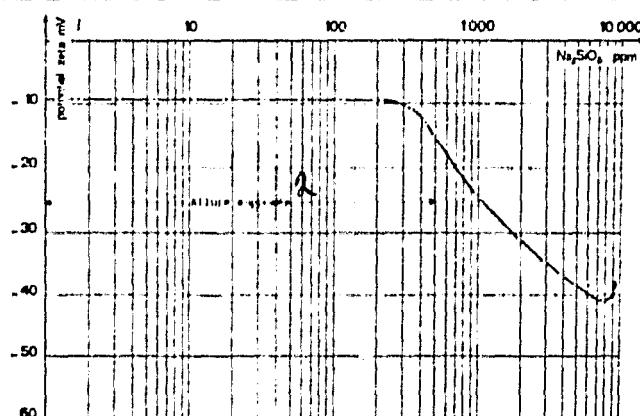


Plate 8. Ball Clay Hyplas 64. Deflocculation curves.
Key: 1-Zeta potential 2-Assumed aspect.

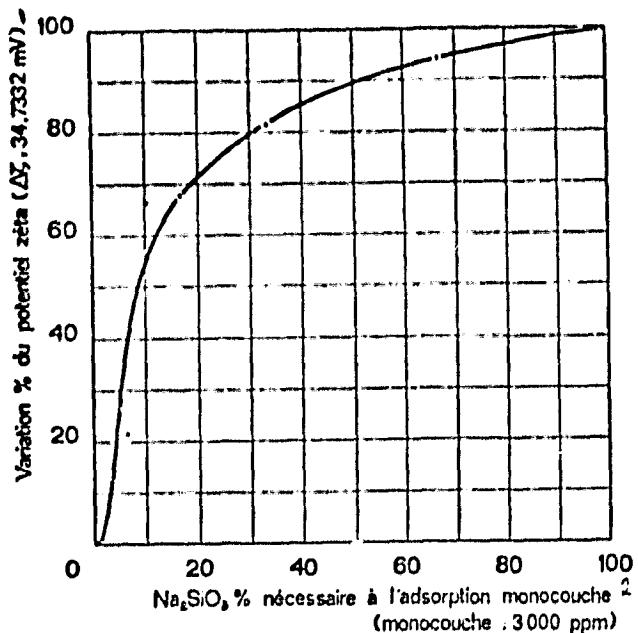


Plate 7. Kaolin d'Arvor.
Density 1300 g/l.

Key: 1-% Variation of zeta potential 2-% necessary
for monolayer adsorption (monolayer: 3000 ppm).

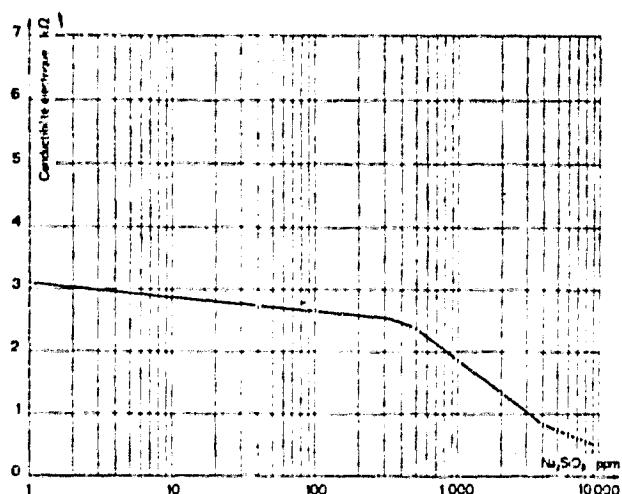


Plate 9. Ball Clay Hyplas 64.
Electrical conductivities.

Key: 1-Electrical conductivity.

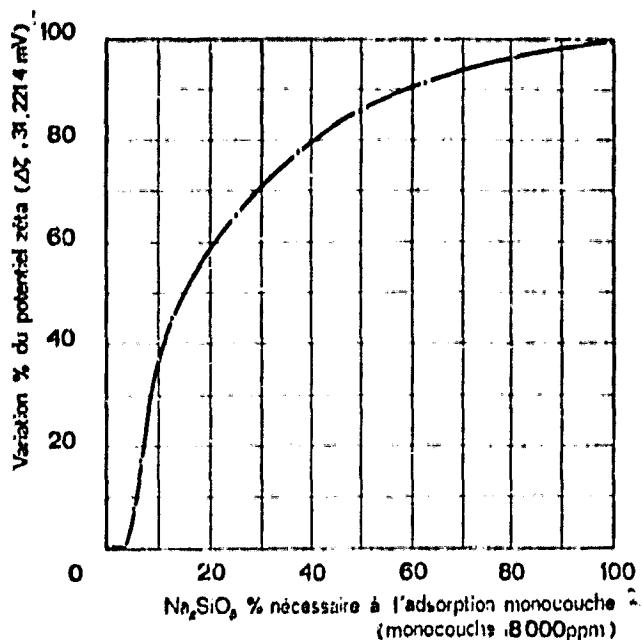


Plate 10. Ball Clay Hyplas 64,
Density: 1300 g/l.

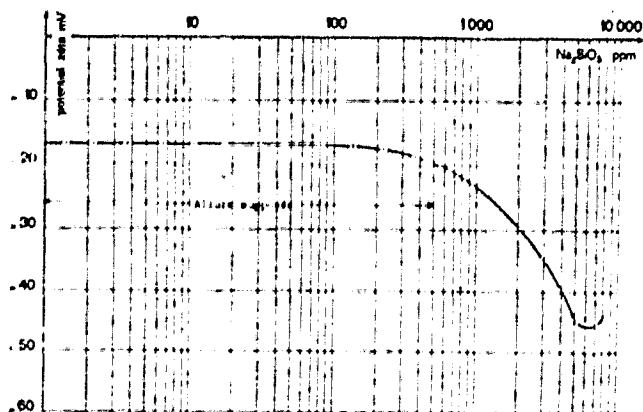
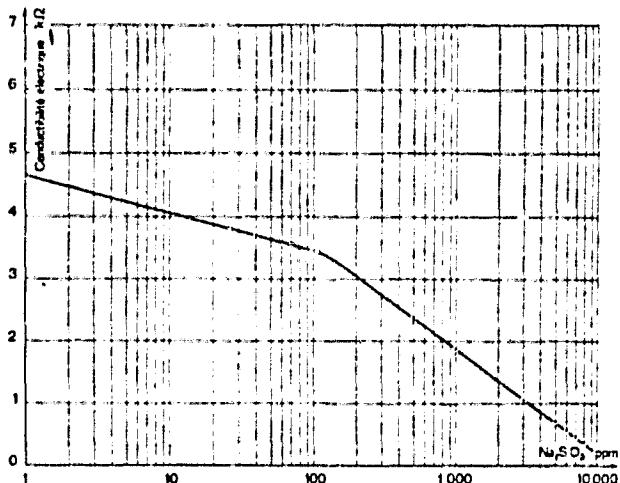
Key: 1-% variation of zeta potential 2-% necessary
for monolayer adsorption (monolayer: 8000 ppm).

TABLE 6. BALL CLAY HYPLAS 64.
SLIPS: 1300 g/l.

Na ₂ SiO ₃ ppm	R _m Ω	w _e 10 ⁻⁴ cm s ⁻¹ /v cm ⁻¹	B _m 10 ⁻³ v
0	3110,50	—	—
40	2712,25	—	—
100	2669,75	—	—
500	2387,75	1,06	15,36
1000	1874,75	1,67	24,15
2000	1337,75	2,11	30,42
3000	1103,75	2,39	34,27
4000	814,60	2,57	36,80
5000	738,32	2,62	38,54
6000	671,22	2,64	38,49
7000	632,25	2,61	30,07
8000	566,62	2,91	41,22
9000	506,85	2,85	39,04

TABLE 7. GRANGER CLAY NO. 10.
SLIPS: 1300 g/l.

Na_2SiO_3 ppm	R_m Ω	α_r $10^{-4} \text{ cm s}^{-1} \text{ V cm}^{-1}$	β 10^{-3} V
6	4659.17	-	-
40	3706.25	-	-
100	3462.10	-	-
500	2375.70	1.46	19.92
1000	1876.50	1.87	25.80
2000	1167.75	2.10	29.53
3000	1044.80	2.54	34.70
4000	782.82	2.89	39.45
5000	705.95	3.16	44.97
6000	571.92	3.14	44.39
7000	469.87	3.29	45.55
8000	390.85	3.23	44.16

Plate 11. Granger Clay No. 10.
Deflocculation Curve.Plate 12. Granger Clay No. 10.
Electrical Conductivities.

Key: 1-Electrical conductivity.

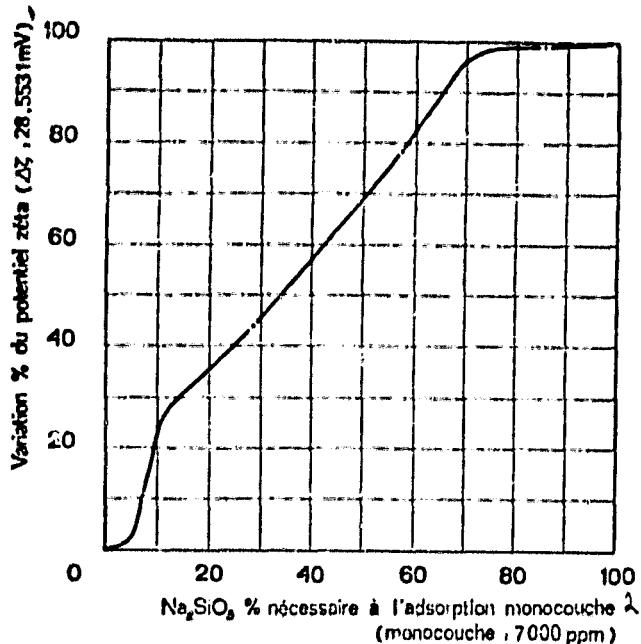


Plate 13. Granger Clay No. 10.
Density 1300 g/l.

Key: 1-% variation of zeta potential 2-% necessary
for monolayer adsorption (monolayer: 7000 ppm).

714. Facts Observed-Interpretations

7141. Densities-Zeta Potential

The various measurements carried out both on deflocculated slips and those non-deflocculated, Kaolin d'Arvor slip, demonstrate that the density is a very influential parameter on the zeta potential value.

Indeed, for the same experimental conditions, same current, same passage time, the mean distance covered by an argillaceous particle from one electrode to the other is even greater when the density of the slip is large from the single fact of the number of particles present. It is clearly evident that a particle will have even more ease in "tracing out a path" when the number of neighboring particles will be low.

Consequently, the electrophoretic velocity will itself be larger and consequently, the zeta potential higher.

The zeta potential thus increases when the density of the slip decreases, this increase being even more regular when the density is low. The remark made in paragraph 7111 is not valid at high densities.

7142. Minimum of Deflocculation Curves

We observe on all the curves a minimum corresponding to a maximum deflocculation. There is identity of this minimum with that recorded on the viscosity-silicate concentration curves. /31

The quantity of deflocculant introduced, in ppm, for this optimum deflocculation is independent of the density, the deflocculant/dried materials weight ratio is constant but remains difficult to discern with precision from the fact of the limited number of manipulations. It approximates:

- 2500 to 3000 ppm for Kaolin d'Arvor;
- 7000 ppm for Granger Clay No. 10;
- 8000 ppm for Ball Clay Hyplas 64.

On this side of this point, we assist with progressive deflocculation; below it, frictions between particles and surrounding liquid containing cations in excess tend to delay movements toward the anode, the electrophoretic velocities thus decrease and consequently, the zeta potential also.

7143. Classification of These 3 Primary Materials

Conforming with the classification of M. Riddick, the three primary materials merge, at the same density, into the same class:

$$-41 < \zeta < -60 \text{ mV} \text{ good stability (section 123).}$$

Nevertheless, we note that this stability decreases from kaolin d'Arvor $\zeta=53.00$ mV to Ball Clay Hyplas 64 $\zeta=41.22$ mV, passing through Granger Clay $\zeta=46.45$ mV.

We also note that the quantity of silicate introduced varies in in-

verse sense from 2500 to 8000 ppm.

At this, a single possible explanation with the present state of our knowledge in this realm: the specific surface-we will return there.

Note: comparisons between values of magnitudes ω_e and ζ in the paragraphs: 7151, 7152 and 7153 agree in absolute value and not relative.

72. Binary Mixtures

Of the following compositions (in % dried materials).

TABLE 8.

Barbotines ¹	Kaolin d'Arvor	Ball Clay Hyplas 64	Argile ² Granger n° 10	Densité ³ Mat. Séchées
A	39	50	—	2,638 8
B	—	50	50	2,644 9
C	50	—	50	2,624 0

(see diagram, plate 14)

Key: 1-Slips 2-Granger Clay No. 10 3-Dried materials density.

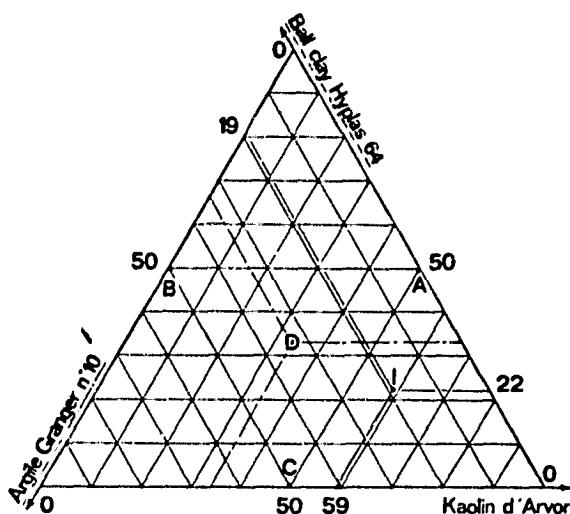


Plate 14. Compositions of argillaceous slips.

Key: 1-Granger Clay No. 10.

721. Slip A (2638.8 g/cm³) (table 9; plates 15 and 16)

TABLE 9. SLIP A.
Dried materials densities: 2638.8 g/cm³
Slip densities: 1300 g/l

Na ₂ SiO ₃ ppm	R _m Ω	ε _r 10 ⁻⁴ cm s ⁻¹ /v cm ⁻¹	β 10 ⁻³ v
1000	2320	-	-
2000	1505	-	-
3000	1022,50	2,76	38,76
4000	836,60	3,06	43,30
5000	651,22	3,26	45,00
6000	564,50	3,36	46,45
7000	497,90	3,30	46,19
8000	415	3,30	45,35

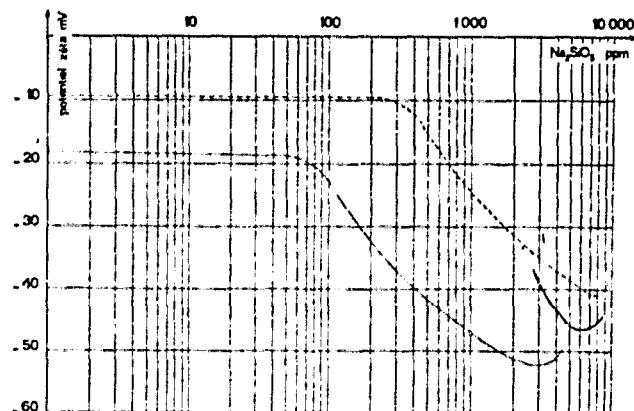


Plate 15. Slip A.

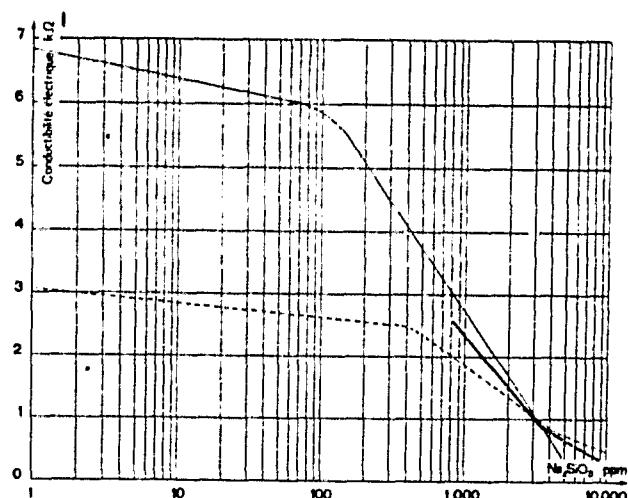


Plate 16. Slip A.
Key: 1-Electrical conductivity.

TABLE 10. SLIP B.
Dried materials densities: 2644 g/cm³
Slip densities: 1300 g/l

Na ₂ SiO ₃ ppm	R _m Ω	v _t 10 ⁻⁴ cm s ⁻¹ /v cm ⁻¹	v 10 ⁻³ v
2000	1251	~	~
3000	1068,25	~	~
4000	797,50	2,69	36,49
5000	694,97	2,87	39,00
6000	530,77	2,84	40,08
7000	519,82	3,02	42,57
8000	487,20	3,11	42,83
9000	411,50	2,91	40,43

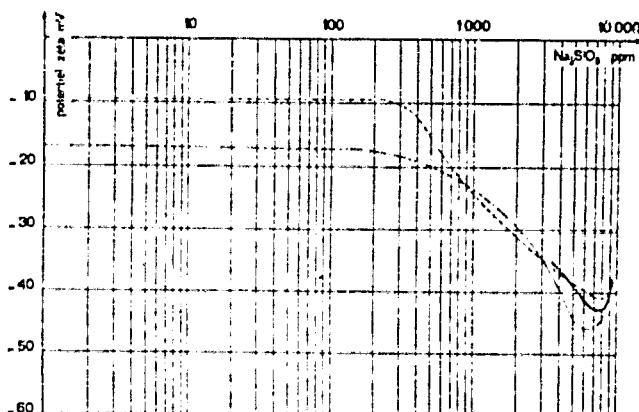


Plate 17. Slip B.

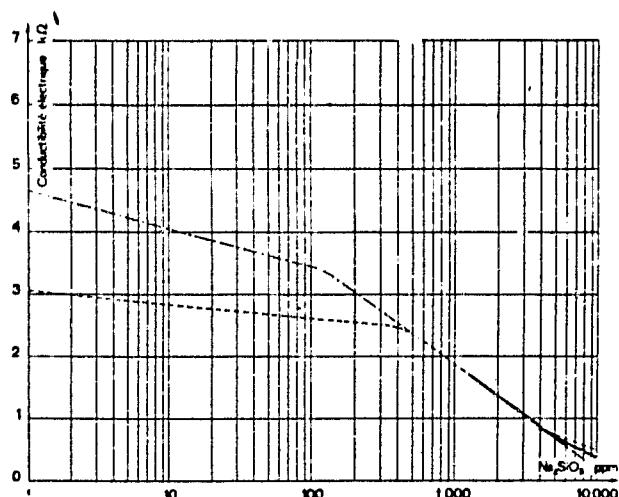


Plate 18. Slip B.

Key: 1-Electrical conductivity.

723. Slip C (2624.0 g/cm³) (table 11; plates 19 and 20)

TABLE 11. SLIP C.
Dried materials densities: 2624 g/cm³
Slip densities: 1300 g/l

Na ₂ SiO ₃ ppm	R _m Ω	ε _r 10 ⁻⁴ cm s ⁻¹ /v cm ⁻¹	ε 10 ⁻³ v
1000	2352,40	2,21	31,41
2000	1552,60	2,65	37,21
3000	1100	2,93	41,65
4000	787,22	3,30	45,52
5000	628,52	3,58	49,28
6000	462,27	3,31	46,87

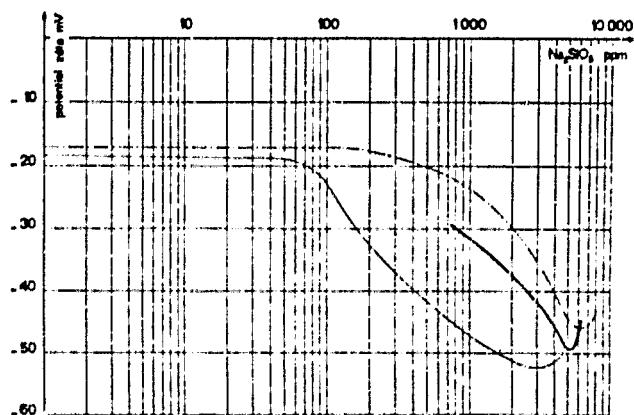


Plate 19. Slip C.

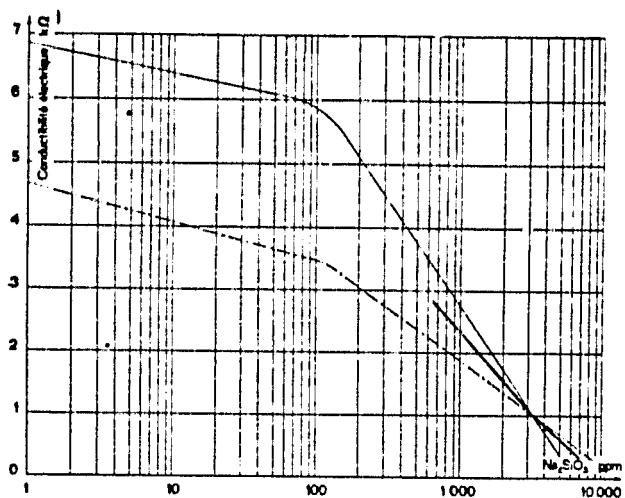


Plate 20. Slip C.

Key: 1-Electrical conductivity.

7241. Aspect of the Deflocculation Curves

If the deflocculation curves present aspects similar to those seen previously, it is emphasized that the values with which they have been constructed are not simply deduced from the values obtained for the primary materials alone.

The zeta potential value of a mixture of argillaceous materials does not follow a simple law, but is governed by a more complex law which can not presently be able to be clarified more by measurement.

Nevertheless, we note that it probably finds its origins in the following two points:

- the surface charges of the particles, different according to the nature itself of these particles, which carry along interactions of electrostatic origin;
- intrinsic characteristics of the minerals in suspension, clearly the specific surface and morphology.

7242. Electrical Resistances

It appears, in relation to them, that they strictly follow a simple additive law, which a priori appeared logical and which is confirmed later, with close measurement errors.

73. Ternary Mixtures

From the following compositions (in % of dried materials).

TABLE 12.

Barbotines ¹	Kaolin d'Arvor	Ball Clay Hyplas 64	Argile ² Granger n° 10	Densité ³ Mat. Sèches
D	33,3	33,3	33,3	2,636 9
I	59	22	19	2,629 4

Key: 1-Slips 2-Granger Clay 3-Dried materials density.

731. Slip D (2635.9 g/cm³) (table 13; plates 21 and 22)

TABLE 13. SLIP D.
Dried materials densities: 2635.9 cm³
Slip densities: 1300 g/l

NH ₄ SO ₄ ppm	R _m Ω	η _{r,l} 10 ⁻⁴ cm s ⁻¹ /V cm ⁻¹	B ₁ 10 ⁻³ V
1000	2150	—	—
2000	1437	—	—
3000	1272,25	2,82	40,10
4000	906,80	2,91	41,17
5000	791,95	3,01	43,27
6000	651,80	3,18	45,42
7000	531,97	3,06	43,91

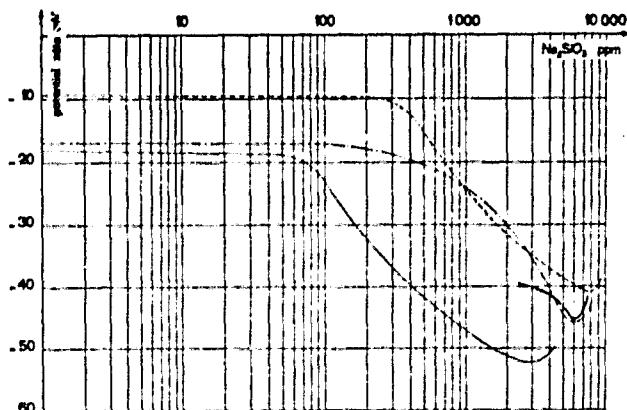


Plate 21. Slip D.

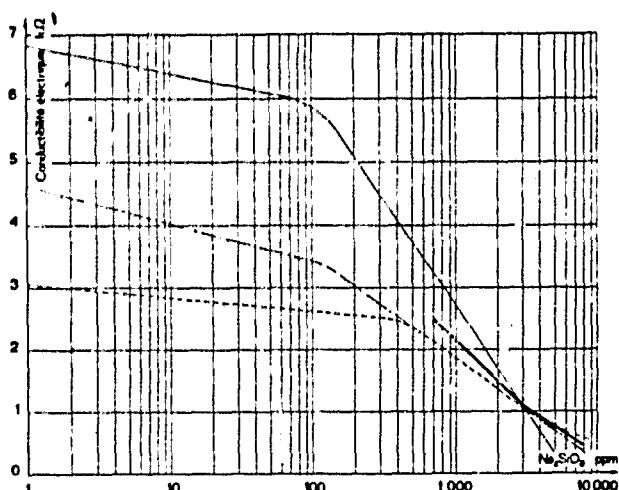


Plate 22. Slip D.

Key: 1-Electric conductivity.

TABLE 14. SLIP I.
 Dried materials densities: 2629.4 g/cm³
 Slip densities: 1300 g/l

Na_2SiO_3 ppm	R_m Ω	$10^{-4} \text{ cm s}^{-1} \text{ V cm}^{-1}$	10^{-3} v
1000	2558,75	2,49	35,40
2000	1477,25	2,79	39,99
3000	1207	3,06	43,12
4000	887,22	3,23	45,62
5000	733,92	3,37	47,08
6000	556,87	3,37	46,88
7000	475,05	3,18	45,47

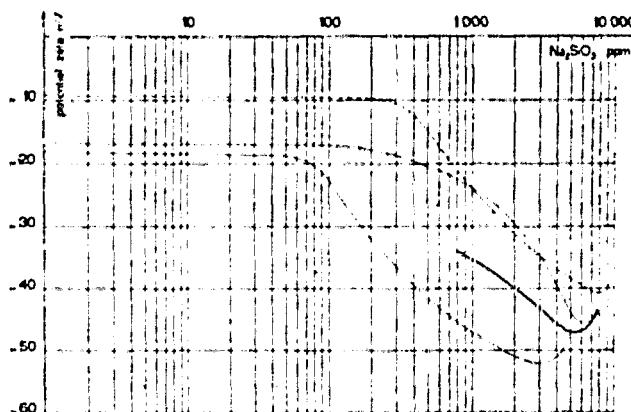


Plate 23. Slip I.

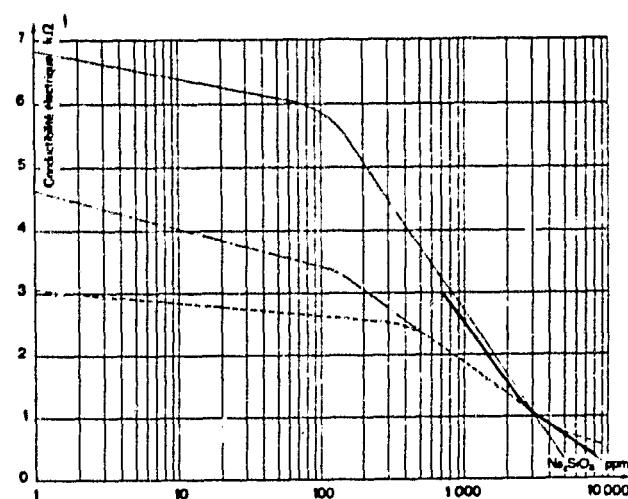


Plate 24. Slip I.

Key: 1-Electric conductivity.

This slip of a priori "bizarre" composition reconstitutes in fact and at first approximation the argillaceous phase of an industrial type casting slip of name: Slip I.

733. Facts Observed-Interpretation

The remarks made previously both on the aspect of the deflocculation curves and on the electrical resistances are completely applicable to these two compounds.

Nevertheless, we will note in relation to slip I that the pre-dominant character of kaolin d'Arvor, here in high proportion (59%) translates perfectly into the curves obtained, particularly on the electrical conductivity.

8. Significance of the Specific Surface

/35

81. Facts Observed (Table 15)

TABLE 15.

Matières sèches ¹	Surfaces ² spécifiques m ² /g
Kaolin d'Arvor	8,40(*)
Argile Granger n° 10 ³	21,30(*)
Ball Clay Hyplas 64	30,10(*)
Barbotine A ⁴	19,25
" B	25,70
" C	14,85
" D	19,93
" I	19,62

* S.F.C. measurements by the BET method, the other values having been obtained by calculations, proportional to the concentrations of the different primary materials.

Key: 1-Dried materials 2-Specific surfaces 3-Granger Clay No. 10 4-Slip.

We place, for each of the slips studied, primary materials alone, binary mixtures, and ternary mixtures, under the same experimental conditions, with 100% deflocculation.

We will see, not only that the zeta potential increases when the specific surface decreases, but that besides, this variation is perfectly linear.

Indeed, by application of the least squares method to this series of values, it becomes:

$$\zeta = -0.336 \sigma + 56.754$$

where: ζ is expressed in mV
 σ in m^2/g .

This expression giving again the values measured within approximately 1.4% due to the shape of the specific surface: to predict, for a primary argillaceous material of known specific surface, under the experimental conditions given, the value of the electrokinetic potential with optimum deflocculation and the corresponding deflocculant concentrations.

Hence indeed, the same least squares method applied to the electrolyte concentration gives:

$$\text{Na}_2\text{SiO}_3 = 245.89 \sigma + 1231.38 \quad (\text{plate 25})$$

where: Na_2SiO_3 is expressed in ppm
 σ in mg^2/g

If we now locate ourselves at 80, 60, 40 and 20% of deflocculation for each of the slips studied, we will see that the straight line observed at 100% curves little by little from 80 up to 20% of deflocculation (plate 26).

The limited number of measurements does not allow us to calculate the equations from them.

82. Interpretations

The electrokinetic potential thus increases linearly when the specific surface decreases (at 100% of deflocculation), whereas the electrolyte concentration increases.

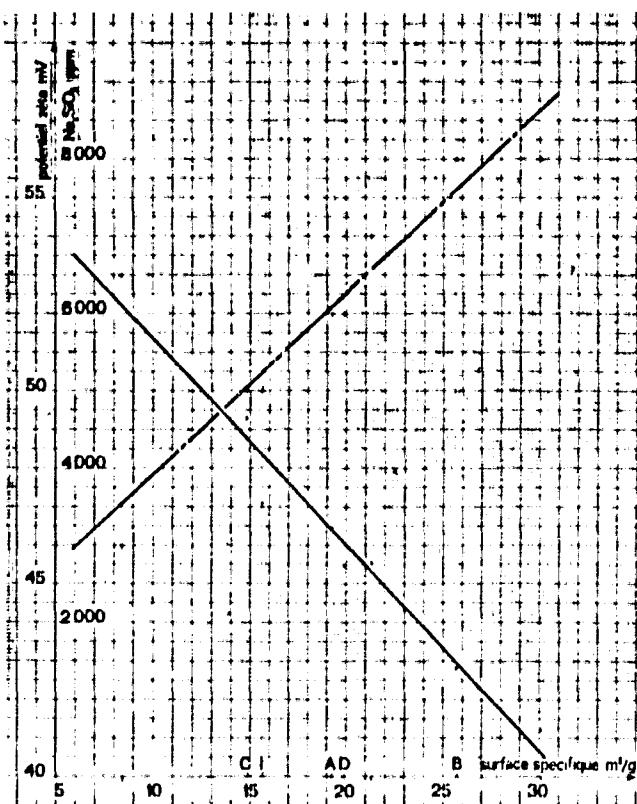


Plate 25. Zeta potential-specific surface.

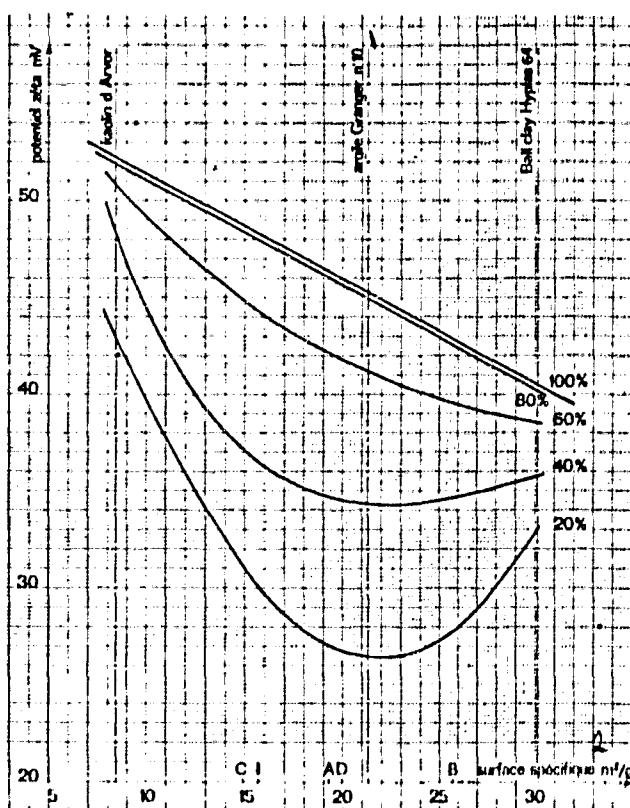


Plate 26. Zeta potential-specific surface
Key: 1-Granger Clay 2-Specific surface.

The deflocculation resulting from progressive adsorption of the electrolyte in solution by the argillaceous particles, we easily know that with large specific surface corresponds to a higher rate of electrolyte and reciprocally.

That the zeta potential decreases when the specific surface increases can only be explained by taking into account electrostatic forces prevailing within the slip. /37

With large specific surface corresponds a large number of particles thus with more numerous and stronger interactions, but also more complex. Inversely, with small specific surfaces would correspond to lower number of particles thus with weaker interactions, and consequently higher electrostatic velocities, as a result of also higher electrokinetic potentials.

Note: a study of the respective morphology of each of the primary materials studied and their mixtures was conducted very conclusively to the confirmation of this hypothesis.

9. Conclusions

From this study, there result the following seven fundamental points:

- 1-the zeta potential is not an intrinsic characteristic of the mineral, but of the suspension formed by the mineral dispersed in solution.
- 2-the zeta potential is a direct function of the density of the slip studied, an even more regular function when the density is low, of the type $\zeta = aP^2 + bP + c$.
- 3-the zeta potential of a slip passes through a corresponding maximum and with optimum deflocculation and minimum viscosity, for a proportion of deflocculant independent of the density.
- 4-an argillaceous slip is even more stable when its zeta potential is high.
- 5-the zeta potential value of a slip constituted of a mixture of primary argillaceous materials does not follow a simple law, but is governed by a more complex law which we still ignore.

6- the maximum zeta potential of an argillaceous slip appeared to be in close relationship with the specific surface of the argillaceous material constituting it. The relationship was then linear:

$$\zeta = a\sigma + b$$

The two parameters a and b depending on the deflocculant used and being equal respectively to -0.536 and 56.754 for sodium silicate Sinet A.

7-the proportion of deflocculant corresponding to this maximum was also a linear function of the specific surface:

$$\tau = a'\sigma + b'$$

The two parameters a' and b' depending on the deflocculant used and being equal respectively to 245.89 and 1231.38 for this same silicate.

10. Critique of the Method

/37

Like any method, determination of the zeta potential on the apparatus available at S.F.C. offers advantages and disadvantages.

Besides that it allows direct study of very rich dispersions in dispersed phase, which constitutes its major interest, we can attribute to it qualities of reliability and relative ease of use for seemingly low acquisition costs.

Subsequently, reproaches are made in regard to the manipulation itself, long and tedious, average time per measurement: 1 hour (this time includes preparation of the slip), it requires very great vigilance at the level of the cleanliness of the apparatus; cleanliness which conditions the value of the measurement since the principle is of the double weighing, which explains why we can not reduce to less than three the number of manipulations for determination of an accurate and consistent value of the zeta potential.

This compensating for that, this apparatus can respond to the requirements of routine work contributing at once to the formulation and control of dispersions (overall precisions: from 1 to 3%).

11. Perspectives

If this study had responded completely to the problems posed, which we repeat were:

- objective and precise limits of the possibilites and capabilities of the "Electrophoretic Mass Transport Analyzer";
- attribution of a significant and useable value of the zeta potential with argillaceous slips;

it only constitutes a prelude to the studies to come:

- studies for which we will be able to precisely define the immediate large lines;
- systematic study of numerous other argillaceous materials; study of the zetameter, but also study of the morphology (scanning microscopy);
- study of the influence of the specific surface at different states of deflocculation;
- research on parameters a and a', b and b' for electrolytes other than silicate.

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